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(21) International Application Number: PCT/SE91/00329 (22) International Filing Date: 8 May 1991 (08.05.91) (30) Priority data: 9001707-0 11 May 1990 (11.05.90) SE (71) Applicant (for all designated States except US): PLM AB [SE/SE]; Djäknegatan 16, S-201 80 Malmö (SE). (72) Inventors; and (75) Inventors/Applicants (for US only) : FRANDSEN, Erik [DK/DK]; Syvhojvej 130, Dk-5260 Odense S (DK). MAZZONE, Rolando [DK/DK]; Strandgyden 27, DK- 5466 Asperup (DK). (74) Agent: MAGNUSSON, Gustav, L.; Magnupatent, Gustav Magnusson AB, Post Box 6207, S-200 11 Malmö (SE).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i>
(54) Title: POLYMER MATERIAL AND A PROCESS FOR ITS PRODUCTION (57) Abstract <p>The disclosure relates to a polymer material and a process for its production. The polymer material consists of partially split polyamide and the process entails that an optional polyamide is caused to react with a nucleophilic reagent under melting conditions.</p>		

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POLYMER MATERIAL AND A PROCESS FOR ITS PRODUCTION.

The present invention relates to a polymer material with increased reaction sensitivity.

- 5 In the plastics and polymer sectors, considerable work and resources have been devoted to the development of plastic materials capable of preventing thermal degradation during processing, for example by oxidation or the influence of UV radiation. As a rule, these stabilizing effects are achieved by additives to polymers.
- 10 However, within the plastics sector there are also needs for non-stabilized plastics material, i.e. plastics material with increased reaction sensitivity. One such need is satisfied in that, according to the present invention, there is provided a polyamide-based material which consists of a partially split or broken down polyamide. The term
- 15 "partially split" or "partially broken down" imply that a fraction of the molecules and/or the groups in the polyamide chain have become dissociated, with a restructuring as a consequence. According to the present invention, this increased reaction sensitivity is employed and the present invention finds practical application within all areas in
- 20 which the absence of compounds or substances with chemical affinity to the split polyamide is advantageous.

- As non-restricting examples of fields of application for the polymer material according to the present invention, mention might be made of
- 25 construction material for panels, containers (trays, cans, bottles, etc), sheets, foils, caps etc. In most cases, the increased sensitivity of the material to reaction with oxygen, i.e. its affinity to oxygen is employed by causing a space which it is intended to exclude from the action of an oxygenaceous environment, to be surrounded by
- 30 walls or other defining means including the polymer material. As one among many examples, mention will be made of a container (package) for perishable goods which deteriorate if they are exposed to oxygen (for example coffee). The entire container or package need not, naturally, consist of the material, it being quite sufficient if the container
- 35 displays one layer thereof.

According to one preferred embodiment, the polymer material is present as a "masterbatch" to which, prior to forming into objects of, for instance, the above-described type, is added other polymer or polymers, possibly together with conventional additives (fillers, reinforcing agents, colourants, etc). It will readily be perceived that the mixing process will be facilitated if both the polymer material according to the present invention and the polymer or polymers which are to be admixed display the same physical form, such as granulate form. Thereby, it will thus be possible in a very simple manner to impart to polymer materials properties which they did not originally possess. This increases flexibility in the choice of materials, at the same time as both raw materials costs and manufacturing costs may be controlled. The explanation for this is that it has proved, at least in certain practical applications (for example in packages) that a quantity of "masterbatch" amounting to 5 weight-% or less will be fully sufficient to achieve the contemplated results.

The polymer material according to the present invention has been obtained by partial splitting of a polyamide. The polyamides which are subjected to partial splitting are commercially available and may be of both aromatic and aliphatic nature. So-called copolyamides, i.e. copolymers of polyamides and other polymers are also suitable starting materials for the partial splitting.

One preferred aromatic polyamide (as starting material) is a polymer which has been obtained by polymerization of meta-xylylene-diamine of the formula $\text{H}_2\text{NCH}_2\text{-m-C}_6\text{H}_4\text{-CH}_2\text{NH}_2$ and adipic acid of the formula $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$, for example a product manufactured and marketed by Mitsubishi Gas Chemical Company, Japan, under the designation MXD6. Preferred polyamides of aliphatic nature are nylon 6 (PA 6) and nylon 6.6 (PA 66). The choice of polymer is not critical, being rather determined by economic factors.

According to one preferred embodiment, the above-mentioned partial splitting is realized in that a polyamide is caused to react with a nucleophilic reagent, possibly in the presence of an activator, preferably under the melting conditions of the polyamide.

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According to a further embodiment, the above-mentioned partial splitting is realized in that a polyamide is subjected to thermal degradation, for example in an extruder (under melting conditions).

- 10 According to one preferred embodiment, the polymer material according to the invention is, thus, produced in that a polyamide is caused to react with a nucleophilic reagent, possibly in the presence of an activator in the form of a hydrogen donor, under such conditions that a uniform homogeneous polyamide product or an unhomogeneous polyamide
- 15 product is obtained. According to yet a further preferred embodiment, the reaction is carried out in an extruder in which the reaction temperature, during at least part of the reaction, exceeds the melting temperature of the polyamide component. In such instance, the polyamide is present in granulate form or powder form (particulate form),
- 20 while the nucleophilic reagent and the possible activator are present in granulate form, as powder or as a liquid. The choice of the nucleophilic reagent and, where applicable, the activator, is critical inasmuch as the nucleophilic reagent and the activator must be stable up to the melting point of the polyamide component.

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- As preferred examples of the nucleophilic reagent, the following might be mentioned: compounds containing at least one carboxylate group, compounds containing at least one amino group, compounds containing at least one hydroxyl group, compounds containing at least one alkoxide
- 30 group, phosphate compounds, pyrophosphate compounds, or polyphosphate compounds. According to one preferred embodiment, the nucleophilic reagent consists of a copolymer of vinyl alcohol and ethylene (EVOH). As activator (hydrogen donor), use may be made of any optional activator, but with the proviso that this is stable up to the melting
- 35 point of the polyamide component. As preferred examples, mention might be made of compounds containing at least one carboxyl group, such as polycarboxylic acids, dicarboxylic acids, or simple carboxylic acids.

One preferred aliphatic carboxylic acid is adipic acid, and one preferred aromatic carboxylic acid is phthalic acid (together with their isomers). Fatty acids, such as stearic acid have proved to be very appropriate. An extremely appropriate activator according to the present invention is marketed under the trade name "Admer QF 551".

A person skilled in this art will readily perceive that the nucleophilic reagent and the activator may be selected from a large number of compounds, but that this number is drastically restricted as a consequence of the requirement on stability at the melting point of the polyamide. A guiding value of the melting point (for selection of "stable" reagent) is approx. 250 °C, with variations in both directions by roughly 10 °C. The stability requirement may also be expressed such that the nucleophilic reagent and, where applicable, the activator must have a retained capacity to react with the polyamide at temperature conditions around the melting temperature of the polyamide.

As was mentioned above, the selection is made according to one preferred embodiment, of the nucleophilic reagent from among carboxylates, amines, alcohols and phosphate compounds. As representative examples of compounds within these categories and while observing the stability requirement, mention might be made of ionomeric materials of such types as are marketed under the trade mark "Surlyn"; salts of organic acids such as calcium stearate; tetraethylene pentamine; polyethylene glycol 400 or 600; EVOH and tetrasodium phosphate.

As was mentioned above, the polymer material according to the invention is present, in one preferred embodiment, as a masterbatch to which is added other polymer or polymers, these latter often being designated matrix or structure polymers. As a non-restrictive quantity interval for the split polyamide, mention might be made of from 1-15 weight-%, smaller quantities being, however, as a rule preferred, ideally within the range of between 1 and 5 weight-%.

As non-restrictive examples of matrix or structure polymers, mention might be made of polyethylene terephthalate (PET), polyethylene,

polypropylene and polyamide. In order to improve homogeneity, use is made in certain cases of a so-called compatibilizer, for example an ionomer of Surlyn type.

- 5 Prior to admixing in the structure polymer, there is incorporated therein, according to one embodiment, an activating metal (oxidation catalyst), such as Co, Fe, Mn, Cu etc, for example in that the structure polymer is mixed in granulate form with a salt of the metal and the thus treated granules are processed (compounded) in an
10 extrusion moulding machine and granulated once again.

- According to another embodiment, there is incorporated, prior to admixing in the structure polymer, an activating metal (oxidation catalyst), such as Co, Fe, Mn, Cu, etc in the partially split poly-
15 amide, for example in the same way as in the case of the structure-polymer, as has been described above. In this embodiment, the master-batch must be protected from the effects of oxygen from production to use, for example by being packed in bags of aluminium foil.

- 20 According to yet a further embodiment, no active admixture of metal compound takes place in the structure polymer, reliance being instead placed on those residual quantities of metal which are already present in the polymer and which derive from catalysts employed in the manufacture of the structure polymer. The granules of the structure poly-
25 mer and the granules of the split (activated) polyamide are thereafter mixed in suitable proportions.

- The mixing of structure polymer and polyamide is suitably effected in that each of the components is mixed in the molten state. For example,
30 both of the polymers may initially be present individually as granules or pellets. Each one of the components is washed separately and thereafter physically mixed in a suitable device possibly with additives. After possible drying, a substantially uniform polymer melt mixture is achieved. A suitable method of forming the "mixture" is by melting-
35 extrusion. In the extruder, the polymers are mixed in the molten state and, thereafter, the mixture is extruded in the form of a strand which, after "hardening", may be cut or otherwise comminuted to

granules or pellets which may thereafter be formed into objects in a conventional manner. The temperature in the extruder is adapted to the properties of the polymers and is, as a rule, between 200 and 400 °C, suitably between 230 and 300 °C and preferably between 240 and 270 °C.

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The present invention will be explained in greater detail hereinbelow, with reference to non-restrictive examples.

EXAMPLE I

10 Production of partially split polyamide (masterbatch)

Granulate of nucleophilic reagent (e.g. Sellar OH 3003 (EVOH), 10 weight-%), possible activator (e.g. Admer QF 551, 2 weight-%) and polyamides (e.g. MXD6 6001, remainder) were mixed and extruded using
 15 an extruder (AXON, type BX-25) with single screw and five heating zones (235-245 °C, 240-250 °C, 240-250 °C, 240-250 °C, 250-260 °C), in the form of strands which were subsequently comminuted in a granulator. The thus produced granulate was dried at 70 °C for 4-5 hours
 20 and air-tight packed in bags of aluminium foil.

The above example was repeated, with the exception that the following nucleophilic reagents were used in a concentration of between 1 and 15 weight-%, together with the polyamides listed below. In those cases
 25 when an activator was employed, this consisted of "Admer QF 551" and was added in an amount of between 1 and 2 weight-%. The polyamide constituted the remainder.

Example	Nucleophilic reagent	Activator	Polyamide
30 2	EVOH	Yes	PA6
3	EVOH	Yes	PA6.6
4	Polyethylene glycol 400	Yes	MXD6
5	Polyethylene glycol 600	Yes	MXD6
6	Polypropylene glycol 425	Yes	MXD6
35 7	"Surlyn 1706"	-	MXD6
8	"Surlyn 1706"	-	PA6
9	"Surlyn 1706"	-	PA6.6
10	Tetrasodium diphosphate	-	MXD6

In order to evaluate the reaction propensity to oxygen, containers were produced from a mixture of PET and each respective polyamide produced according to examples 1-10. In certain cases, the PET employed was "doped" with cobalt (approx. 150 ppm) and the weight relationship between PET and polyamide was approx. 95:5. The containers (1.5 l) were manufactured by conventional blow moulding. Each container was subjected to so-called OTR measurement (Oxygen Transmission Rate) according to standards. OTR is expressed in cc/24h. In all experiments, a value of below 0.001 was obtained.

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For containers produced from 100% PET and PET/MXD6 (95:5) OTR values of 0.08 and 0.05, respectively, were measured.

CLAIMS

1. A polymer material with increased sensitivity to reaction with oxygen, c h a r a c t e r i z e d in that it consists of partially split polyamide.
- 5 2. The material as claimed in claim 1, c h a r a c t e r i z e d in that it consists of the reaction product of a polyamide and a nucleophilic reagent and possibly an activator in the form of a hydrogen donor.
- 10 3. The material as claimed in claim 2, c h a r a c t e r i z e d in that the nucleophilic reagent consists of a compound containing at least one carboxylate group, a compound containing at least one amino group, a compound containing at least one hydroxy group, a
15 compound containing at least one alkoxide group, or consists of a phosphate, pyrophosphate or polyphosphate compound.
- 20 4. The material as claimed in claim 3, c h a r a c t e r i z e d in that the nucleophilic reagent consists of copolymer of vinyl-alcohol and ethylene (EVOH).
- 25 5. The material as claimed in anyone of claims 2-4, c h a r a c - t e r i z e d in that the activator is a compound containing at least one carboxyl group.
6. The material as claimed in anyone of claims 2-5, c h a r a c - t e r i z e d in that the nucleophilic reagent and the activator are stable up to the melting point of the polyamide.
- 30 7. A process for producing a polymer material with increased sensitivity to reaction with oxygen, c h a r a c t e r i z e d in that a polyamide is caused to react with a nucleophilic reagent, possibly in the presence of an activator in the form of a hydrogen donor under such conditions that a uniform, homogeneous
35 polyamide product or an unhomogeneous polyamide product is obtained.

8. The process as claimed in claim 7, characterized in that the polyamide, the nucleophilic reagent and the possible activator are present in granulate form, or as powder, and that the reaction is undertaken in an extruder.

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9. The process as claimed in claim 7 or 8, characterized in that the reaction temperature during at least a part of the reaction exceeds the melting temperature of the polyamide component.

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10. The process as claimed in anyone of claims 7-9, characterized in that the nucleophilic reagent and the activator are stable up to the melting point of the polyamide.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00329

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 G 69/48, C 08 L 77/00														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black;">Classification System</th> <th style="border: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; vertical-align: bottom;">C 08 G; C 08 L</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched⁸</div> <p>SE DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	C 08 G; C 08 L								
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IPC5	C 08 G; C 08 L													
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; border: 1px solid black;">Category *</th> <th style="border: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 10%; border: 1px solid black;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;"> Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 90-069636/10, TOY080 KK: "Polyamide resin compsn. with good gas barrier property etc. - comprises xylene gp.contg. polyamide and modified vinyl aromatic-olefin block copolymer", JP 2020555, A, 900124, 9010 (Basic) -- </td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-10</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;"> WO, A1, 8906664 (ALLIED-SIGNAL INC.) 27 July 1989, see the whole document -- </td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-10</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;"> Chemical Abstracts, volume 107, no. 26, 28 December 1987, (Columbus, Ohio, US), Anon.: "Heat treatment of amorphous nylon to improve oxygen barrier ", see page 36, abstract 237796e, & Res.Disc1., 1987, 279, 418 -- ----- </td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-10</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 90-069636/10, TOY080 KK: "Polyamide resin compsn. with good gas barrier property etc. - comprises xylene gp.contg. polyamide and modified vinyl aromatic-olefin block copolymer", JP 2020555, A, 900124, 9010 (Basic) --	1-10	A	WO, A1, 8906664 (ALLIED-SIGNAL INC.) 27 July 1989, see the whole document --	1-10	A	Chemical Abstracts, volume 107, no. 26, 28 December 1987, (Columbus, Ohio, US), Anon.: "Heat treatment of amorphous nylon to improve oxygen barrier ", see page 36, abstract 237796e, & Res.Disc1., 1987, 279, 418 -- -----	1-10
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>^a Special categories of cited documents: ¹⁰</p> <p>^{"A"} document defining the general state of the art which is not considered to be of particular relevance</p> <p>^{"E"} earlier document but published on or after the international filing date</p> <p>^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>^{"O"} document referring to an oral disclosure, use, exhibition or other means</p> <p>^{"P"} document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>^{"X"} document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>^{"Y"} document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>^{"&"} document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 28th June 1991 </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 1991-07-30 </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">SWEDISH PATENT OFFICE</div> </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Sofia Nikolopoulou</div> </td> </tr> </table>			Date of the Actual Completion of the International Search 28th June 1991	Date of Mailing of this International Search Report 1991-07-30	International Searching Authority <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">SWEDISH PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Sofia Nikolopoulou</div>								
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ANNEX TO THE INTERNATIONAL SEARCH REPORT

ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 91/00329

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 8906664	89-07-27	AU-D- 3050589	89-08-11
		EP-A- 0397767	90-11-22
		US-A- 4826955	89-05-02